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An effective method of controlling metal particle size on impregnated Rh-Mn-Li/SiO_2 catalyst

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A convenient and effective impregnation method was found to prepare Rh-Mn-Li/SiO_2 catalyst by using large granularity of silica as support, of which Rh particle size is at 2–4 nm with narrow distribution and the number of it accessible for reagents is enhanced. As expected, the space-time yield (STY) and selectivity of C_{2+}oxygenates were significantly increased from 338.6 g/kg-cat.h, 49.2% to 618.4 g/kg-cat.h, 54.6% respectively, when 14–20 mesh, instead of 20–40 mesh of silica, was employed.

KEY WORDS: particle size effect; impregnation method; Rh-based catalyst; C_2-oxygenates; CO hydrogenation.

1. Introduction

The catalytic hydrogenation of carbon monoxide has attracted much attention in the past decades, mainly due to the growing demand for oxygenated products, particularly C_2 oxygenates such as ethanol, acetaldehyde, acetic acids and/or esters [1–4]. Many research activities have been carried out in order to acquire the knowledge about the influence of the catalyst nature on the catalytic behavior. Among others, the metal particle size is of great importance because CO hydrogenation is a structure-sensitive reaction [5,6]. Reactions involving either C–C bond breaking or formation are usually structure sensitive, and this implies that the formation of supported particles with proper size is critical to enhance the catalytic activity and selectivity to C_2-oxygenates [7]. In the case of impregnated catalysts, the particle size has usually been controlled by changing metal loading [8] or by sintering at high temperature, or even by changing the pore structure of supports [9,10]. So far, the Rh-Mn-Li/SiO_2 catalyst, usually prepared by impregnating method, is proven to be one of the most promising catalyst systems for the synthesis of C_2 oxygenates from syngas. Thus, the controlling of Rh particle size is very important to obtain high performance Rh-based catalyst. Changing Rh loading to obtain proper particle size leads to high metal loading (ca. 4.7 wt.%) and low Rh efficiency [8]. Employment of silica with appropriate pore size achieves desirable average metal particle size on impregnated catalyst, but the size distribution might be broad. In addition, calcining at high temperature makes metal particles grow up or embed and results in low Rh dispersion. Furthermore, it is noteworthy that metal loading, pore structure of silica and calcination also directly affect the catalytic reaction by themselves. Unfortunately, this effect was neglected in these literatures when they discussed the particle size effect on catalytic behavior. In order to exclude the latter effect mentioned above, the identical support, the same Rh loading and the same activation are applied in the present work, and then we attempt to regulate only impregnation-related impact factor, such as granularity of silica, to achieve satisfactory Rh particle size distribution on Rh-Mn-Li/SiO_2 catalyst. Finally, CO hydrogenation reaction was used to evaluate its activity for the formation of C_2-oxygenates.

2. Experimental section

Rhodium chloride was provided by Johnson Matthey Precious Metal Company. The catalysts were prepared by conventional co-impregnation of various pellet size of SiO_2 (BET surface area 205.2 m^2/g, average pore diameter 17.7 nm, Haiyang Chemicals Plant) with an aqueous mixture solution of $RhCl_3$, $Mn(NO_3)_2$ and $LiNO_3$ (Tianjin Chemical Agents Third Plant). Three types of silica were used: 40–60, 20–40 and 14–20 mesh, corresponding to catalyst K40, K20 and K14, respectively. Such catalysts were dried at 383 K for 20 h. Rh loading of all catalysts was 1.0 wt.% and the weight ratio of Rh:Mn:Li was 1:1:0.075.

The transmission electron microscopy (TEM) measurements were carried out using a HITACHI H600 microscope operated at an accelerating voltage of 50 kV. The catalysts before testing were reduced in pure H_2 at 623 K for 1 h. The samples were then ultrasonically suspended in ethanol and placed onto a carbon film supported over a copper grid. The sizes and shapes of catalyst particles were obtained by analyzing the TEM images. The size distribution of Rh particles was

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drawn as an average profile of the accessible particles during the measurements.

Transmission infrared spectra of adsorbed CO were obtained by a BRUKER EQUINOX 55 single-beam FT-IR spectrometer. All spectra were recorded with 16 scans with a resolution of 4 cm^{-1}. The sample was first reduced in flowing H_2 at 573 K for 1 h. After reduction, the catalyst was evacuated at 573 K for 30 min, then cooled to room temperature and introduced CO (10 Torr) for 2 min. The gaseous CO was pumped out for 7 min before the spectrum was recorded.

All the catalysts were *in situ* activated by H_2 (623 K, 1 h) before reaction. CO hydrogenation was carried out in a fixed-bed microreactor (316 l, 300 mm length and 4.6 mm inner diameter) under 593 K, 3.0 MPa (H_2/CO = 2) and GHSV = 12500 h^{-1}. The effluent gas passed through a condenser filled with cold de-ionized water and was subsequently analyzed online chromatographically. The produced oxygenates were completely dissolved in water and were analyzed off-line by Varian 3800 GC with an HP-FFAP capillary column, *n*-pentanol as an internal standard. Each time 1 ml catalyst was used.

3. Results and discussion

Figure 1 demonstrates the TEM photography of the K40, K20 and K14 catalysts. It can be seen that the Rh nanoparticles are highly dispersed, especially for sample K14, with similar round shapes. The Rh particle size distribution is obtained by the statistic calculation from all the TEM images, and the mean crystallite size is thus estimated. As shown in figure 2, the narrowest Rh particle size distribution is observed on sample K14 and the Rh size is 2–4 nm (average particle size ca. 2.9 nm). For sample K40, most crystallite size is centralized at ca. 2.5 and 5.0 nm (average particle size ca. 4.0 nm), as well as 1.5 and 2.9 nm for sample K20 (average particle size ca. 2.7 nm). It discloses that large pellet size of support used helps to achieve catalyst with sharp Rh size distribution between 2 and 4 nm.

Three types of CO adsorbed species, gem-dicarbonyl (2100, 2030 cm^{-1}), terminally (2060 cm^{-1}) and bridged (1853 cm^{-1}), are existed over all samples (see figure 3). It is found that the band produced over catalyst K14 is the most intense suggesting that metal crystallite is better dispersed on this catalyst surface, in agreement with TEM result, and thus more CO adsorbed chemically on Rh particle. Accordingly, we conclude that the number of Rh particle accessible to reactant molecules increases during CO hydrogenation reaction.

Performance of CO hydrogenation over sample K40, K20 and K14 is listed in table 1. Sample with pellet size of 20–60 mesh is employed to eliminate internal diffusion effect (the influence of external diffusion is negligible due to high GHSV applied in this experiment). Catalyst K20, prepared from 20–40 mesh of silica, exhibits normal catalytic performance, as indicated that space-time yield (STY) and selectivity of C_{2+} oxygenates are 338.6 g/kg-cat.h and 49.2%, respectively. When 40–60 mesh of silica is employed, the resulting catalyst K40 displays higher STY (417 g/kg-cat.h) for the formation of C_{2+} oxygenates. However, STY of C_{2+} oxygenates quickly reaches 618.4 g/kg-cat.h with 54.6% selectivity when pellet size of support increases up to 14–20 mesh. Thus it can be seen that the use of large size of silica to prepare impregnated catalyst dramatically increases the catalyst activity for the formation of C_2-oxygenates, improving Rh efficiency to the high level, which is the best result reported in the literature up to now.

On the other hand, it is noticed that CO conversion continuously increases from 7.9 to 11.6% with the support granularity, as well as the selectivities of methanol and ethanol, but acetaldehyde selectivity decreases

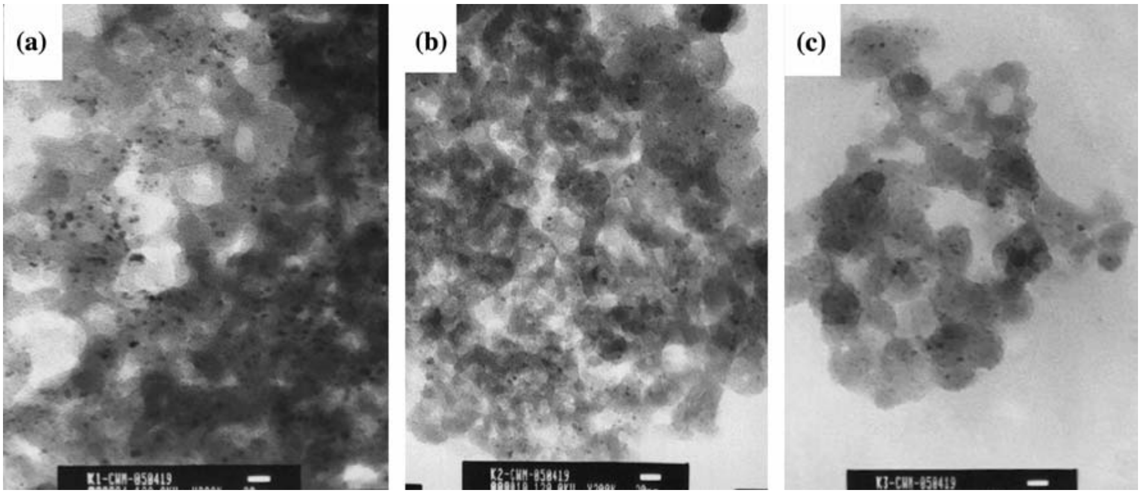

Figure 1. TEM photography for various catalysts prepared by different pellet size of silica: (a) K40; (b) K20; and (c) K14.

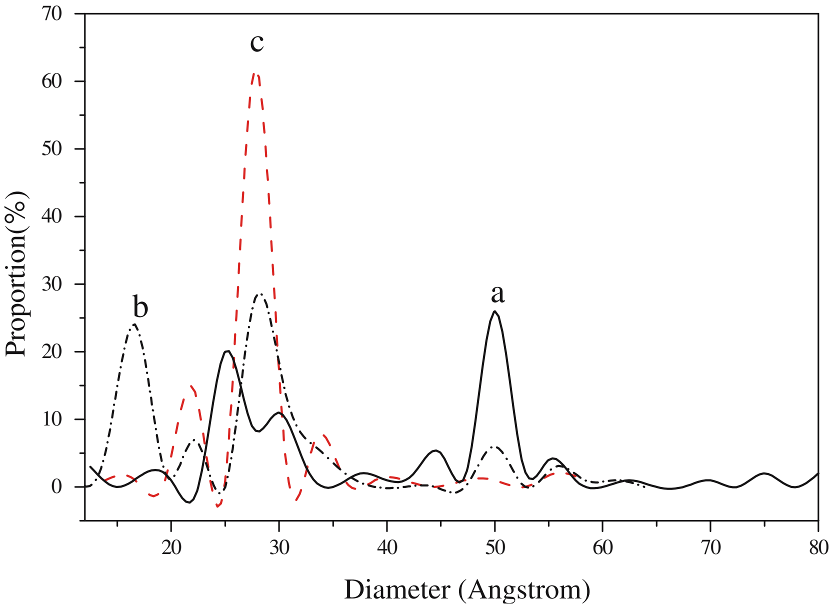

Figure 2. Rh particle size distributions over Rh-Mn-Li/SiO_2 catalysts prepared by different pellet size of silica: (a) K40; (b) K20; and (c) K14.

slightly. Nevertheless, a small increase in the selectivity towards methane is accompanied by a decrease in the selectivity to C_{1+} (hydrocarbons other than methane). According to the well-known C_2-oxygenates formation mechanism [11,12], it would be reasonable to deduce from the evolution of product distribution that elemental step of hydrogenation was promoted, while insertion reaction of CH_x to produce long-chain hydrocarbons was restrained when catalyst is prepared using 14–20 mesh of support.

CO hydrogenation results of catalyst K14 with different pellet size are given in table 2. Little change in catalytic performance is observed when catalyst pellet size varied from 40–60 to 20–40 mesh. However, there is an evident decrease in catalyst activity when sample size reaches 14–20 mesh, indicating that considerable internal mass-transfer resistance exists. Therefore, it is suitable to keep the sample size at 20–60 mesh (preferablely 20–40 mesh) in our reactor. It is also found that the selectivities towards C_2-oxygenates, methanol, ethanol and acetaldehyde decline notably while the selectivities to acetic acid and C_{1+} (hydrocarbons other than methane) increase abruptly under internal diffusion-rate-controlling condition. As

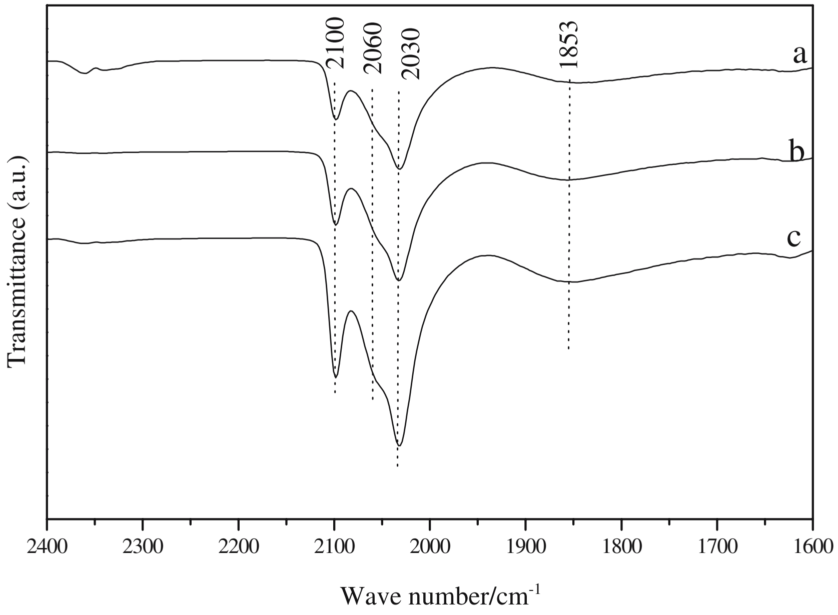

Figure 3. IR spectra of absorbed CO over Rh-Mn-Li/SiO_2 catalysts prepared by different pellet size of silica: (a) K20; (b) K40; and (c) K14.

Table 1
Effect of silica size during impregnating on CO hydrogenation performance over Rh-Mn-Li/SiO_2 catalysts

	Concentration of carbon (%)	Y_{C_2+oxy} (g/kg-cat/h)	Selectivity of products, carbon (%)						
			C_{2+oxy}*	CH_4	C_{1+}	MeOH	EtOH	AcH	HOAc
K40	7.9	417.1	50.1	34.6	15.0	0.3	11.9	25.3	7.3
K20	8.4	338.6	49.2	36.7	13.8	0.3	13.4	23.7	6.0
K14	11.6	618.4	54.6	37.6	7.3	0.5	19.0	23.2	6.8

Reaction conditions: 593 K, 3.0 MPa (H_2/CO = 2) and GHSV = 12500 h^{-1}.
*C_{2+oxy} implies oxygenates containing two or above carbon atoms, the same below.

Table 2
Effect of catalyst granularity on CO hydrogenation performance of catalyst K14

Catayst size (mesh)	Concentration of carbon (%)	Y_{C_2+oxy} (g/kg-cat/h)	Selectivity of products, carbon (%)						
			C_{2+oxy}	CH_4	C_{1+}	MeOH	EtOH	AcH	HOAc
40–60	11.4	584.8	55.4	36.9	7.3	0.4	18.9	23.5	6.8
20–40	11.6	618.4	54.6	37.6	7.3	0.5	19.0	23.2	6.8
14–20	10.9	489.4	47.1	35.0	17.8	0.1	11.8	20.2	9.8

Reaction conditions: 593 K, 3.0 MPa (H_2/CO = 2) and GHSV = 12500 h^{-1}.

stated above, it can be inferred that insertion reaction of CH_x is favored, whereas the insertion of CO into alkyl group and the CH_x or other group hydrogenation reaction are suppressed. It is likely that the diffusion rate of CO and H_2 into catalyst surface is limited and gives rise to the decline in surface coverage of non-dissociated CO molecular and dissociated H atom.

Hanaoka [13] found an optimal Rh particle size between 2 and 4 nm for the formation of C_2-oxygenates from syngas over Rh/SiO_2 catalysts. Accordingly, among the three Rh-Mn-Li/SiO_2 catalyst (Rh = 1.0 wt.%) without calcination prepared from the same silica, the most active for C_2-oxygenates synthesis over sample K14 is attributed to narrower crystallite size distribution and more dispersed Rh particles accessible for reactant on the catalyst surface, although mean particle size on all catalysts is in the range of 2–4 nm. The reason of this striking influence of pellet size of silica employed on the Rh particle size distribution is still unclear and will be investigated in future.

4. Conclusion

The impregnated Rh-Mn-Li/SiO_2 catalyst with sharp metal particle size distribution between 2 and 4 nm can be handily prepared by using 14–20 mesh of silica without changing metal loading and different pore size of support or any calcination. Such catalyst displays highly active for the formation of C_2 oxygenates from syngas.

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